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# Simulation of Epichlorohydrin Synthesis from Dichloropropanols in Reactive Distillation Column Using Aspen Plus

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**ABSTRACT**

*Epichlorohydrin is an important raw material for the production of epoxide resins, synthetic elastomer, sizing agents for paper-making industry and so on. The reactions involved in the production of epichlorohydrin from dichloropropanols (DCP), including 1,3-dichloro-2-propanol and 2-3-dichloro-1-propanlol have been kinetically investigated by other researcher. Based on those kinetics parameter we have tried to design a suitable reactor for dehydrochlorination reaction and have tried to chose the optimum operating conditions. The present paper discusses the simulation work on reactive distillation for the production of epichlorohydrin using ASPEN PLUS. The reactive distillation can offer substantial benefits compared with conventional reaction-separation-recycle system. The simulation results have been verified with the data published by others. The influence of operating condition on the yields of epichlorohydrin has been also investigated.*

**Keywords**

*reactive distillation; epichlorohydrin; simulation; aspen plus; dichloropropanol*

## 1. INTRODUCTION

The synthesis of epichlorohydrin from dichloropropanols has become increasingly important because epichlorohydrin is an intermediate raw material in the production of epoxide resins, synthetic elastomer, sizing agents for paper-making industry, and water treatment. Additionally, dichloropropanol, as a raw material of epichlorohydrin synthesis, can now be prepared easily from crude glycerol which has abundance availability because of biodoesel booming [2]. For this synthesis, aqueous sodium hydroxide (NaOH) reacts with 1,3-DCP according to Equation 1. In such a reaction medium the epichlorohydrin (EPY) formed may be converted to glycerol (GLY), as shown in equation 2, resulting in lower yield of EPY [2],[6]. For this reason, EPY must be removed from the reaction environment as quickly as possible. To overcome this problem in conventional method, EPY product is stripped with steam in a distillation column and the contact time must be short to minimize hydrolysis.[6]. However, these processes have some problems in yield and overall costs. Therefore, developing an preliminary design of RD unit for synthesis of EPY would be a challenging work.

The reactive distillation is a hybrid process that combines the reaction and separation in a single equipment which is combines the functionality of a continuous reactor with a conventional distillation process. The product is retired at the same it is formed

Basically, RD has several advantages including increase conversion, improve yield, improve selectivity for complex reaction, better heat control, and reduces the overall costs [1],[3],[5].

$$C_3H_6Cl_2O + NaOH \rightarrow C_3H_5ClO + NaCl + H_2O \quad (1)$$

$$C_3H_5ClO + NaOH + H_2O \rightarrow C_3H_8O_3 + NaCl \quad (2)$$

Aspen Plus, sequential modular simulator, contains an extensive model library that allows most unit operations to be simulated easily and accurately. Implementation of model equations and all simulation were carried out using the model RADFRAC from the steady-state simulator Aspen Plus which is based on a rigorous equilibrium stage model for solving the material balance, vapor-liquid equilibrium, mole fraction and heat balance equations. To validate the reactive distillation model, the simulation results are compared with experimental results published by S. Carr (1979) and also published by Ma et al. (2007) for synthesis of EPY.

## 2. MODELING AND SIMULATION RESULT

Key feature of the simulation include the vapor-liquid equilibrium calculations. For all the reaction systems, UNIFAC model was used for the calculation for activities and Hayden O´Connell equations for fugacities (considering that the system are 1,2-DCP, 1,3-DCP, EPY, GLY, and water)

## 2.1. Vapor Liquid Equilibria

The system examined includes water, 1,2-DCP, 1,3-DCP, EPY, GLY, $Ca(OH)_2$ and $CaCl_2$. Since the process is carried out at about 1 atm, the vapor-liquid equilibrium constants for volatile components can be written as

$$\frac{y_I}{x_I} = K_I = \frac{p_I^o \gamma_I}{P} \quad (1)$$

In the above equation it is assumed that the most significant deviations from ideality are present in liquid mixtures.

The vapor pressure of different species are expressed by the Antoine's equation as below

$$ln\, p_i^o = \frac{A_I}{T} + B_I \quad (2)$$

The parameters of the equation are summarized in Table 1, together with the values of the vaporization enthalpies ($\Delta H_{ev}$)

Where:

$x_i, y_i$ = liquid vapor mole fraction of component i
$K_i$ = equilibrium ratio of component i
$p^o_i$ = vapor pressure of component i
$\gamma_I$ = activity coefficient of component i
$A_i, B_i$ = Antoine's constant of component i

**Table 1 Parameters of Eq 2**

| Compound | $A_i$ | $B_i$ | $\Delta H_{ev}$ Kcal/mol | ref |
|---|---|---|---|---|
| 1,3-DCP | 6181 | 20.58 | 12.238 | a-d |
| 1,2-DCP | 6775 | 22.15 | 13.410 | e |
| EPY | 4847 | 19.06 | 9.597 | a |
| GLY | 5738 | 19.81 | 11.361 | d |
| $H_2O$ | 5118 | 20.376 | 10.220 | f |

[a]Stull (1947), [b] Auschnitz and Ritter (1955), [c] Kahlbaum (1945), [d] Kahlbaum (1954), [e] Experimental, [f] Reid and Sherwood (1958)

## 2.2. Simulation Result

The columns were simulated using Aspen Plus, which used rigorous algorithms for reactive distillation calculations. The generalities and conditions are summarized as follow:

- Reaction in liquid phase and modeling with chemical equilibrium.
- For the calculate of distribution coefficients (Ki) was use a model with activity and fugacity coefficients evaluate by UNIFAC and Hayden O'Connel equation, respectively.

**Table 2 Specifications simulated reactive distillation column**

| Operative conditions | |
|---|---|
| Number of stages | 20 |

| | |
|---|---|
| Feed plate | 2° |
| Rectification section stages | 1-5 |
| Stripping section | 15-20 |
| Column pressure (constant pressure along the column) | 101.325 kpa |
| Feed composition 1,3-DCP | 0,11 |
| $H_2O$ | 0,889 |

**Table 3. Experimental [6] and simulated results**

| Top Composition | Experimental | Simulated |
|---|---|---|
| $x_{1\text{-}3DCP}$ | 0.0042 | 0.00228 |
| $x_{EPY}$ | 0.024 | 0.03928 |
| $x_{H2O}$ | 0.9718 | 0.95844 |

S.Carra et. al (1979)[6], reported some experimental runs were made in a micropilot plant. It was constituted by a column with 20 perforated plates, of 8 cm of diameter, and 300 sieves. The column was fed continuosly with the stream having the composition shown in Table 3. A stream of steam was fed at the bottom.

The result of the mentioned runs were simulated using aspen plus in order to validate the reliability of our simulation to describe the amount of EPY present in the distillate. The obtained results are summarized in Table.3. it can be observed that for EPY the situation is satisfactory since the difference between simulated and experimental data is less than 11%.

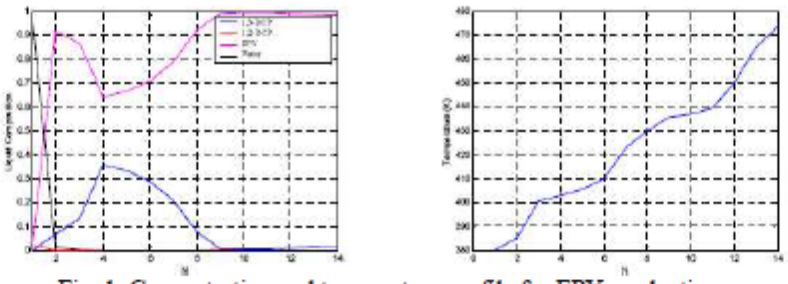

Fig. 1. Concentration and temperature profile for EPY production

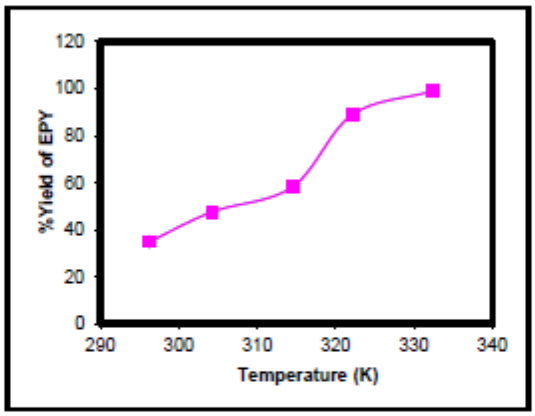


Fig 2. Effect of temperature on Yield of EPY production

Figures 1 shows concentration and temperature profile for epychlorohydrin production. In this case the reactive were consumed totally reached a product purity closed to 95%. Figure 2 shows that trend of the yield of epichlrohydrin is effected by increasing of the temperature.

## 3. CONCLUSION

In the present paper, a simulation study was carried out on the epichlorohydrin production using the Aspen Plus simulation software. Since both chemical reactions and product separation occur in the unit considered, the yields are strongly dependent on the plate volumes, which effect the contact time, and heating rate at the reboiler, and therefore the stripping efficiency of the column. On the whole it seems that aspen plus is valuable for finding the best operating conditions of the process under study.

## ACKNOWLEDGEMENT

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